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Original Research Paper

Synthesis of sulfated zirconia nanopowders via polyacrylamide gel method

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ABSTRACT

In the present study, polyacrylamide gel method was applied for synthesis nanosized sulfated zirconia powders, first time. An assessment of the influence of calcination temperature and sulfate ion loading on the properties of synthesized powders was performed and the samples were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy and thermal analysis. The results revealed that tetragonal phase was obtained on calcination at 500 °C and was stable towards higher temperatures (650 °C). The increase of crystallite size with increasing calcination temperature was observed. Calcination for long duration time led to evolution of some sulfur species, furthermore results in higher particle size ($\sim$100–200 nm) as compared to calcination for short duration time resulting in lower particle size (<50 nm). The presence of sulfate had no significant effect on thermal stability of polyacrylamide gel network whereas structure and the nature of the sulfur species bound with the zirconia surface are affected by the sulfur content.

1. Introduction

Zirconia based ceramics have seen increasing usage due to its unique properties and potential applications [1,2] and when it was modified with anions such as sulfate, exhibits a high catalytic activity [3,4–8]. Concerning stringent environmental requirements, solid catalysts as a suitable substitute for traditional hazardous, corrosive and pollutant liquid acid catalysts can provide environmentally clean processes for the chemical industry. Modified metal oxides with sulfate anion such as sulfated zirconia (SZ), as a solid acid catalyst have gained great interest and become active area of research [6,9,10–14]. Sulfated zirconia has been known to catalyze a variety of reactions such as hydrocarbon isomerization, alkylation and esterification [5,6,15].

In 1962, Holm and Baily were the first to report on the synthesis and catalytic application of sulfated zirconia [16–18]. The activity and selectivity of zirconia catalysts are significantly influenced by preparation method [17,19,20], zirconia catalyst phase [3,6] and other various parameters [3,12,19,20]. Sulfated zirconia exists in three crystallographic structures: monoclinic, tetragonal and cubic [2,21,22], in which only cubic [23,24] and tetragonal [15,21,24] phase of SZ are catalytically active.

Generally, a wide variety of sulfate species exists on sulfated zirconia and several models proposed by authors for sulfate species. Proposed sulfate species involves tridentate bisulfate-like species, mono-dentate bisulfate species and bidentate sulfate [6,25,26]. The nature of the acid sites is still being studied; however, some findings have shown the attribution of acidity of sulfated zirconia to the inductive effect of S=O groups [5,12,27].

Sulfated zirconia so far has been prepared by two different procedures using traditional precipitation technique and sol–gel method [1,9,12,19]. Both of them have their own advantages and disadvantages [7,13,15,28]. The main problems with these methods are irreproducibility [29], non-uniform pore size [7,28], with wider pore-size distributions [15,28] and relatively small surface area [7,15,28]. Notably, these methods lead to formation of nanocrystalline SZ [13,19], however, there are researches which claim that traditional precipitation technique may lead to formation of microcrystalline SZ [1]. In order to improve physical properties of SZ products and overcome some of the problems, modified precipitation and sol–gel methods such as liquid-crystal template (LCT) method [9,28–30], supercritical drying technique [29], and use of mesoporous materials with high surface area as supports [3,10,16,28] have been developed. To gain the advantages of time saving and nanometric scale of synthesized powders, using other modified sol–gel methods such as pechini and polycrylamide

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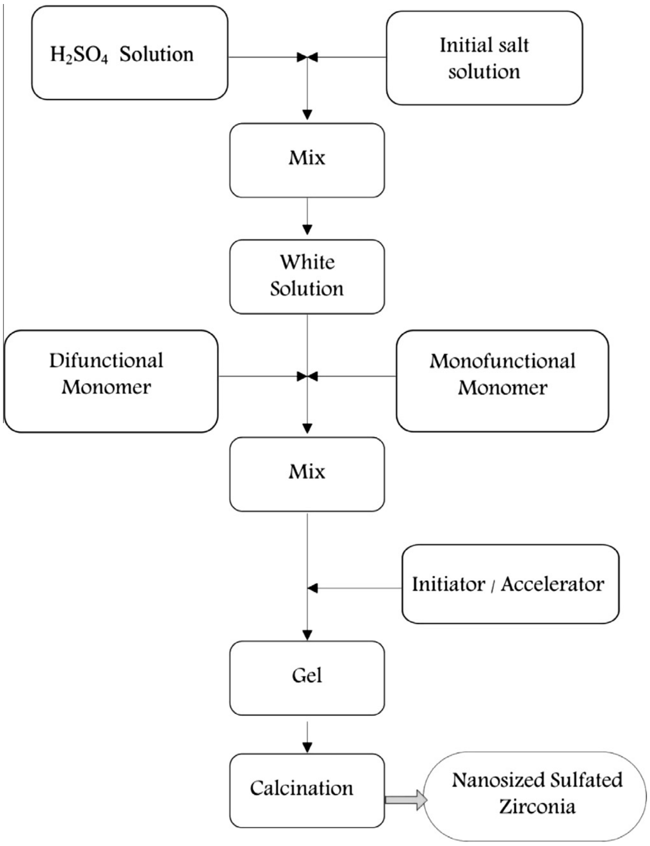

Fig. 1. Synthesis of sulfated zirconia nanoparticles procedure steps by polyacrylamide gel method.

Table 1
Synthesis conditions of the prepared sulfated zirconia samples.

Sample	Calcination temp (°C)	H_2SO_4 concentration (M)	Calcination time in air (h)	Calcination time in argon (h)	v/g[a]	Crystallite size (nm)
SZ1	500	2	2	1	0.1	7
SZ2	550	2	2	1	0.1	7.6
SZ3	600	2	2	1	0.1	8.4
SZ4	650	2	2	1	0.1	13.9
SZ5	550	2	1.5	0.5	0.1	–
SZ6	650	2	1.5	0.5	0.1	–
SZ7	650	0.5	1.5	0.5	0.1	–
SZ8	650	0.5	1.5	0.5	0.0022	–
SZ9	650	1	1.5	0.5	0.045	–

[a] v/g = ml of sulfuric acid/gram of initial salt.

gel methods can be appreciated [31]. The polyacrylamide sol–gel method is a simple, fast and cheap method, in which a solution of the respective cations is soaked. In this method, direct pyrolysis of polymeric network without separate drying step yields very fine and highly dispersed powders. Also, the original materials used in the polyacrylamide gel method are the aqueous solutions of inorganic salts. This allows avoiding use of the expensive metal alkoxides, unlike the other sol–gel methods [22,31].

In our previous works [22,32], nanosized zirconia and α-Al_2O_3 powders were synthesized via poly acrylamide gel method and the effects of various conditions on the nanopowders' properties were studied. The results showed that the presence of impurity ions affects on the stability and thermal behavior of polymeric network and the structural properties of the synthesized powders. To the best of our knowledge, we applied polyacrylamide gel method for first time in the presence of sulfates ions as impurity for synthesis sulfated zirconia. As regards from the viewpoint of catalysis, presence of sulfate groups and crystalline tetragonal phase of zirconia is important. Therefore, the effects of some synthesis parameters such as calcination temperature, calcination time and acid concentration on the presence of sulfate groups, morphology and crystalline structure of the synthesized nanopowders were also investigated. The synthesized samples were characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM), TG-DTA techniques.

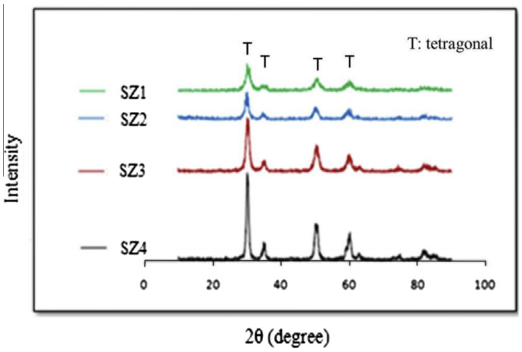

Fig. 2. XRD patterns of the SZ1–SZ4 samples.

2. Experimental

2.1. Materials

The following chemical products were used in the synthesis: zirconium oxychloride; $ZrOCl_2{\cdot}8H_2O$ and sulfuric acid; H_2SO_4 which were used as precursors, acrylamide (AM); $C_2H_3CONH_2$, N,N′-Methylene bis acrylamide (MBAM); $(C_2H_3CONH_2)2CH_2$, ammonium persulfate (APS); $(NH_4)_2S_2O_8$, N,N,N′,N′-tetramethyl ethylene diamide (TEMED); $C_6H_{16}N_2$ which were used as monofunctional monomer, difunctional monomer (crosslinker), initiator and accelerator respectively. All of the materials were supplied by E. Merck, D 6100 Darmstadt, Germany. Also, deionized water was used as solvent.

2.2. Synthesis

The technique used to produce sulfated zirconia in the present work was mainly based on the procedure described by Tahmasebpour et al. [22]. The flow chart of the preparation process is presented in Fig. 1. Zirconium hydroxide was prepared by dissolving 1.33 g of $ZrOCl_2{\cdot}8H_2O$ in 4 ml deionized water. Sulfation procedure was carried out by adding aqueous solution of H_2SO_4 into the prepared solution and was kept in a water bath warmed at 313–333 K for 2 h and then according to procedure that has been described previously [22], 2.42 g of AM and 0.242 g of MBAM monomers with molar ratio of 22 as polymerization agents were added. The free-radical crosslinking copolymerization of AM and MBAM was initiated by adding the initiator system (0.165 ml of APS 10 wt% and 0.405 ml of TEMED 1 wt%) to the mixture. In this state, a white gel was obtained. The obtained xerogel was homogenized in a ceramic mortar and submitted to one subsequent thermal treatment. The xerogel was heated in a laboratory furnace (Ex.1200-2LA) and calcined at different temperatures (500–650 °C). The thermal treatment was applied in a heating rate of 5 °C/min up to the desired holding temperature. Subsequently, the effect of H_2SO_4 concentration at different amount of acid on properties of